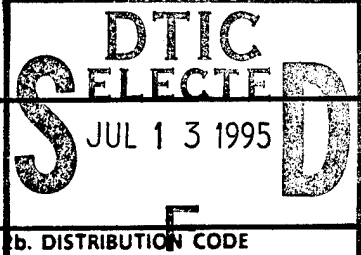


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4. TITLE AND SUBTITLE Surface Chemistry of Non-Fouling Coating Polymeric Materials			5. FUNDING NUMBERS GN0001493310058	
6. AUTHOR(S)  Professor Joseph A. Gardella, Jr.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry, NSM Complex State University of New York, University at Buffalo Buffalo, NY 14260-3000			8. PERFORMING ORGANIZATION REPORT NUMBER  95-06	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Department of the Navy, Office of Naval Research 800 North Quincy St., Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  This document has been approved for public release and sale, its distribution is unlimited.				
13. ABSTRACT (Maximum 200 words) Three phases related to the surface chemistry of potential non-fouling coatings are currently being studied. New analytical methods will be developed for determining fundamental surface structure property relationships, especially for critical micro-structural and bonding details in the topmost surface region. Coordinated surface analytical determination of the effects of structure, processing and treatment will be applied to a variety of multicomponent (especially block and graft co-) polymers. We are cooperating with a number of ONR funded polymer chemists, who are synthesizing new materials with potentially interesting surface properties (K. Wynne, J. Calvert, T. Chapman). New model surfaces with multiple chemical environments need to be synthesized for challenge to questions about the effects of surface and bulk structure on surface properties, specifically bioadhesion or bioabhesion. The study of controlled conformations of model biopolymers on polymeric surfaces by SIMS and HREELS will complete the examination of the fundamentals of the initial stages of biopolymer film formation.				
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OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT N0001493310058

R&T Code 4132083

Surface Chemistry of Non-Fouling Coating Polymeric Materials

Professor Joseph A. Gardella, Jr., P. I.

Department of Chemistry  
State University of New York at Buffalo  
Buffalo, NY 14214-3094

June 20, 1995

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OFFICE OF NAVAL RESEARCH  
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

R&T Number: 4132083

Contract/Grant Number: N0001493310058

Contract/Grant Title: Surface Chemistry of Non-Fouling Coating Polymeric Materials

Principal Investigator: Joseph A. Gardella, Jr.

Mailing Address: 470 NSM Complex, SUNY Buffalo, Department of Chemistry, Buffalo, NY 14260

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3000

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WWW Homepage: [http://www.chem.buffalo.edu/fac\\_res\\_mt/Gardella/index.html](http://www.chem.buffalo.edu/fac_res_mt/Gardella/index.html)

- a. Number of papers submitted to refereed journals, but not published: 6
- b. Number of papers published in refereed journals (provide complete citations): 2
- c. Number of books or chapters submitted, but not yet published: 2
- d. Number of books or chapters published (provide complete citations): 1
- e. Number of printed technical reports/non-refereed papers (provide complete citations): 2
- f. Number of patents filed: 2
- g. Number of patents granted (for each, provide a complete citation): 0
- h. Number of invited presentations (for each, provide a complete citation): 8
- i. Number of submitted presentations (for each, provide a complete citation): 6
- j. Honors/Awards/Prizes for contract/grant employees (list attached): \_\_\_\_\_

(This might include Scientific Society Awards/Offices, Selection as Editor, Promotion, Faculty Award, etc.)

- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number: \_\_\_\_\_

Graduate Students: 8

Post-Doctoral Associates: 1

including the number of,

Female Graduate Students: 1

Female Post-Doctoral Associates: 1

the number of

Minority\* Graduate Students: 1

Minority\* Post-Doctoral Associates: 0

and, the number of

Asian Graduate Students: 3

Asian Post-Doctoral Associates: 0

- l. + Other funding (list agency, grant title, amount received this year, total amount, period of performance and a brief statement regarding the relationship of that research to your ONR grant)

Note: Use the letter and an appropriate title as a heading for your list, e.g.: b. Published Papers in Refereed Journals, or, d. Books and Chapters published. Also submit the citation lists as ASCII files via PC-compatible floppy disks

\* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an under-represented or minority group in science and engineering.

a. Papers Submitted to Refereed Journals

H. Z. Zhuang, K. Gribben-Marra, T. Ho, T. M. Chapman and J. A. Gardella, Jr. "Surface Composition of Fluorinated Poly(amide urethane) Block Copolymers by Electron Spectroscopy for Chemical Analysis", *Macromolecules*, submitted, June, 1995.

C. L. Weitzsacker, J. A. Gardella, Jr. Ch. Grégoire and J. J. Pireaux, "A Quantitative Study of Langmuir Blodgett Model Systems by High Resolution Electron Energy Loss Vibrational Spectroscopy: Spectral Analysis and Sampling Depth", *J. Phys. Chem*, submitted March, 1995.

Y.-Z. Du and J. A. Gardella, Jr. "A Study of the Interaction Between Thermally Deposited Aluminum Films and Fluorinated Polymer Substrates", *J. Vacuum. Sci. Technol., Part A.*, 1995, accepted, in press.

T. Ho, K. J. Wynne, J. A. Gardella, Jr. and H.-Z. Zhuang, "Using Solubility Difference to Achieve Phase Separation in Dimethylsiloxane-Urea-Urethane Copolymers", *J. Coll. Interface Sci.*, 1995, accepted, in press.

P. C. Schamberger, G. L. Jones, J. A. Gardella, Jr. , P. J. McKeown and L. E. Davis "Visualization of a Buried Organic Interface by Imaging ToF-SIMS and Scanning Auger Microprobe of an Ion Beam Crater Edge", *J. Vacuum Sci. and Technol., Part A*, 1995 submitted, in revision.

P. C. Schamberger, J. A. Gardella, Jr., G. L. Grobe, III and P. L. Valint, Jr. "Optimization of Low Temperature Vitrification for Surface Analysis of Hydrated Hydrogel Polymers" *J. Vacuum Sci. and Technol. Part A*, submitted September, 1994.

b. Papers Published in Refereed Journals

X. Chen, J. A. Gardella, Jr., T. Ho and K. J. Wynne, "Surface Composition of a Series of Dimethylsiloxane Urea, Urethane Segmented Copolymers Studied by Electron Spectroscopy for Chemical Analysis", *Macromolecules*, 1995, 28, 1635-42.

J. J. Pireaux, Ch. Grégoire, J. A. Gardella, Jr. and P. A. Cornelio, "Thin Polymer Films on Metal: Assessment of a Conductivity Mechanism Via Valence Band Spectra", Journal of Electron Spectroscopy, Proceedings of ICES-5, International Conference on Electron Spectroscopy, Kiev, Ukraine, July 1993, 1994, 68, 541-546.

c. Books or chapters Submitted

J. A. Gardella, Jr., K. J. Wynne, T. J. McCarthy, J. F. Rabolt and G. Belfort, "New Technologies for Surface Analysis to Assess Biofouling Resistance", Naval Research Reviews, Special Issue on Biofouling, R. Alberte and S. Snyder, Eds., submitted, April, 1995.

J. A. Gardella, Jr. "Secondary Ion Mass Spectrometry", Chapter in The Handbook of Surface Imaging and Visualization, A. T. Hubbard, Ed., CRC Press, accepted, in press, 1995.

d. Books or Chapters Published

K. J. Wynne, T. Ho, R. A. Nissan, X. Chen and J. A. Gardella, Jr. "Polymer Design for Minimally Adhesive Surfaces", Progress in Pacific Polymer Science 3, K. P. Ghiggino, Ed., Springer Verlag, Berlin, 1994, 63-83.

e. Printed Technical Reports/non-refereed papers

K. J. Wynne, T. Ho, A. Vu, X. Chen and J. A. Gardella, Jr., "Toward Minimally Adhesive Polymer Surfaces", Polym. Prepr. Am. Chem. Soc., 1995, 36 (1), 67-8.

H.-Z. Zhuang, J. A. Gardella, Jr., T. Ho and K. J. Wynne "Quantitative Surface Analysis of Solvent Effects on Film Formation of BPAC/DMS Copolymers", PMSE Prepr. Am. Chem. Soc., 1994, 71, 449-50.

f. Patents Filed:

RF 516B Continuation in Part of US Patent # 5,266,309, "Refunctionalized Oxyfluorinated Surfaces", T. G. Vargo and J. A. Gardella, Jr., Co-Inventors.

US Ser No.: 08/354,857 "Fluoropolymeric Substrates with Metallized Surfaces and Methods for Producing the Same" T. G. Vargo, J. M. Calvert, M.-S. Chen and J. A. Gardella, Jr., Co-Inventors.

g. Patents Granted:  
none

h. Invited Presentations by the PI.

"Surface Chemical Analysis of Polymer Materials: Methods and Results", Symposium on Analytical Characterization of Chemically Modified Surfaces, 24th North East Regional Meeting of the ACS, Burlington, VT, June 20, 1994.

"Modification of Polymer Surface Chemistry to Control (Bio) Adhesion: Characterization, Surface Synthesis and Applications", Corning, Inc., Research and Development, Glass and Polymers Group, Corning, NY, July 1, 1994.

"Surface Chemistry of Biomaterials: Some Principles, Characterization, Surface Synthesis and Applications", September 1994 Meeting of the Society for Analytical Chemists of Pittsburgh, Pittsburgh, PA, September 12, 1994.

"Langmuir Blodgett Films as Hierarchical Model Structures for Electron and Ion Spectroscopy", Department of Physics, SUNY Buffalo, Buffalo, NY November 15, 1994.

"Polymer Surface Chemistry: Synthesis, Characterization and Applications in Molecular Biology, Environmental Science and Adhesion", Department of Chemistry, Wayne State University, Detroit, MI, December 6, 1994.

"Polymer Surface Chemistry: Synthesis, Characterization and Applications to Biomaterials", Department of Chemistry, SUNY College at Fredonia, Fredonia, NY, February 2, 1995.

"Analytical Surface Science: Principles and Applications to Polymer Science", Department of Chemistry, St. John Fisher College, Rochester, NY, February 3, 1995.

"Recent Advances in the Design of Polymers Which Minimize Biological Fouling: Synthesis and Surface Chemistry", Laboratoire Interdisciplinaire de Spectroscopie Electronique, Facultés Universitaires Notre-Dame de la Paix, Namur, Belgium, February 22, 1995.

i. Submitted Presentations

R. W. Nowak, J. A. Gardella, Jr. and P. A. Zimmerman "Time of Flight Secondary Ion Mass Spectrometry of Varied Tacticity Langmuir Blodgett Films of Poly (Methyl Methacrylate)", UNY-VAC XXI, 21st Annual Meeting of the Upstate New York Chapter of the American Vacuum Society, Rochester, NY June 9, 1994.

E. J. Bekos and J. A. Gardella, Jr. "Characterization of Surface Modified Poly (hexafluoro-propylene - co-tetrafluoroethylene) as a Biomaterial Substrate", UNY-VAC XXI, 21st Annual Meeting of the Upstate New York Chapter of the American Vacuum Society, Rochester, NY June 9, 1994.

H.-Z. Zhuang, J. A. Gardella, Jr., T. Ho and K. J. Wynne "Quantitative Surface Analysis of Solvent Effects on Film Formation of BPAC/DMS Copolymers", Abstracts of the 208th National Meeting of the American Chemical Society, Division of Polymer Materials Science and Engineering, Washington, DC August, 1994.

J.-X. Chen, X. Chen and J. A. Gardella, Jr. "Surface Modification Studies of Polymer Blends", Abstracts of the 208th National Meeting of the American Chemical Society, Division of Polymer Materials Science and Engineering, Washington, DC August, 1994.

R. W. Nowak, J. A. Gardella, Jr., P. A. Zimmerman and D. M. Hercules, "Time of Flight Secondary Ion Mass Spectrometry Analysis of Langmuir Blodgett Films of Isotactic, Syndiotactic and Atactic Poly (Methyl Methacrylate)", Abstracts of the 41st National Symposium, Applied Surface Science Division, American Vacuum Society, Denver CO, October 24-28, 1994.

E. J. Bekos, F. V. Bright and J. A. Gardella, Jr., "Secondary Ion Mass Spectrometry Studies of Covalently Bound Peptides to a Fluoropolymer: Imaging and Quantitation", Abstracts of the 41st National Symposium, Applied Surface Science Division, American Vacuum Society, Denver CO, October 24-28, 1994.

Y.-Z. Du, R. W. Johnson, Jr. and J. A. Gardella, Jr. "Quantitative Analysis by Static SIMS of Mixed Self Assembled Monolayer Films on Metal Substrates", Abstracts of the 41st National Symposium, Applied Surface Science Division, American Vacuum Society, Denver CO, October 24-28, 1994.

S. M. Kovatch, Y. Kim, E. J. Bekos and J. A. Gardella, Jr. "Static Secondary Ion Mass Spectrometry Study of Amino Acids on Acidic and Basic Polymer Surfaces", Abstracts of the 41st National Symposium, Topical Conference on Biomaterial Interfaces, American Vacuum Society, Denver CO, October 24-28, 1994.

K. J. Wynne, T. Ho, A. Vu, X. Chen and J. A. Gardella, Jr., "Toward Minimally Adhesive Polymer Surfaces", Abstracts of the 209th National Meeting of the American Chemical Society, Division of Polymer Chemistry, Anaheim, CA, April, 1995.

j. Honors/Awards/Prizes for Contract/Grant Employees

J. A. Gardella, Jr.

#### Editorial Boards

CRC Critical Reviews in Surface Chemistry  
Colloids and Surfaces: Part B: Biointerfaces

#### Honors

National Science Foundation Award for Special Creativity 1991-93

#### Scientific Society Offices

Treasurer, WNY ACS Analytical Group/SAS Niagara Frontier Section  
(1990-94)

#### University Elected Chair

SUNY Buffalo Undergraduate College Curriculum Committee and Science Curriculum Subcommittee Member, 1991-1992 **Chair, Curriculum Committee 1992-94.**



## 1. Other Funding

### 1.) Agency: NSF-DMR - Polymers Program

Amount: \$85,000 total costs year 1, \$255,000 total

Title: Ion Beam and Surface Analytical Studies of Macromolecular Surfaces"

Duration: Three Years (8/1/93-7/30/96)

Relationship to ONR Grant: This research program funds fundamental studies in the development of surface analytical measurements to organic and polymeric thin films; in particular using Langmuir Blodgett and self assembled layers to construct a hierarchy of models for polymer surface chemistry. X-Ray photoelectron spectroscopy, Secondary Ion Mass Spectrometry, infrared spectroscopy, contact angle and other microscopic measurements are developed and applied to thin films and multicomponent polymers. There is minor overlap with the ONR award in that both investigate multicomponent polymers. The ONR award benefits from the basic work done under the NSF award.

### 2.) Agency: NATO Travel Grant

Amount: \$11,000

Duration: 4 years (9/1/88-8/31/92)

Title: Sampling Depth in Model Polymers by Electron and Ion Spectroscopies

Co-PI: Professor Jean-Jacques Pireaux, Facultes Universite de Notre Dame de la Paix, Namur, Belgium

Relationship to ONR Funding: This project funded travel between the two laboratories in Buffalo and Namur to perform LB experiments and HREELS and SIMS collaboratively. Funding has ended. The NATO funding is now superceded by ONR travel funding to continue this collaboration to examine HREELS of polymer surfaces.

### 3.) Agency: Bausch and Lomb, Inc.

Amount: unspecified

Duration: unspecified

Title: Support for Daniel Ammon, Ph.D student

Relationship to ONR Funding: This project supports a graduate student jointly studying protein adsorption on hydrogel materials for contact lens applications. The development of a low temperature probe for vitreous samples could have impact on performing "wet, frozen" analysis under the ONR program. No scientific relationship with the ONR grant.

**PROPOSALS SUBMITTED FOR EXTERNAL REVIEW:**

- (i) National Science Foundation Chemistry Division Instrument Program \$1,800,000 3 Years  
"Instrument Development Plan for the Department of Chemistry Instrument Center at SUNY Buffalo" J. D. Atwood, F. V. Bright, L. E. Colón, P. Coppens, J. F. Garvey, J. B. Keister, G. H. Nancollas, Co-PIs.

OFFICE OF NAVAL RESEARCH

END-OF-THE-YEAR REPORT

PART II

for

GRANT N0001493310058

R&T Code 4132083

Surface Chemistry of Non-Fouling Coating Polymeric Materials

- a. Principal Investigator: Professor Joseph A. Gardella, Jr., P. I.
- b. Current Telephone Number: (716-645-6800 X2111 Office, 716-645-6963 FAX)
- c. Cognizant ONR Scientific Officers: Dr. Kenneth Wynne  
Dr. Randall Alberte
- d. Project Description

Three phases related to the surface chemistry of potential non-fouling coatings are currently being studied. New analytical methods will be developed for determining fundamental surface structure property relationships, especially for critical microstructural and bonding details in the topmost surface region. Coordinated surface analytical determination of the effects of structure, processing and treatment will be applied to a variety of multicomponent (especially block and graft co-) polymers. We are cooperating with a number of ONR funded polymer chemists, who are synthesizing new materials with potentially interesting surface properties (K. Wynne, J. Calvert, T. Chapman). New model surfaces with multiple chemical environments need to be synthesized for challenge to questions about the effects of surface and bulk structure on surface properties, specifically bioadhesion or bioabhesion. The study of controlled conformations of model biopolymers on polymeric surfaces by SIMS and HREELS will complete the examination of the fundamentals of the initial stages of biopolymer film formation.

#### e. Significant Results

In the past year, seven projects have been underway under this grant.

1. We have used quantitative angle dependent and low temperature, environmental ESCA to analyze a series of segmented siloxane copolymers synthesized and characterized by Dr. Wynne and Dr. Ho and Dr. Pike. A close collaboration with all has led to the publications submitted.
2. We have applied ToF-SIMS determinations of surface molecular weight distributions to the same series of segmented siloxane polymers. (see research highlight).
3. We have also worked on fluorocarbon polyurethane copolymers Dr. Toby Chapman's research program at Pitt. A full paper has just been submitted on this work, allowing the deconvolution (adapted from and in collaboration with Dr. Ho) of in depth profiles of these materials.
4. We have worked closely with Dr. Gill Geesey's research group in Montana on thin film modification of surfaces, and the study of mussel adhesive protein to controlled structure (siloxane, fluoropolymer) surfaces by ESCA, fluorescence and FTIR.
5. We have also completed a study of solvent casting effects on polycarbonate/siloxane block copolymers by ESCA and FTIR-ATR.
6. We have been focussing on the study of reactive metal interfaces with polymers, extending from fluoropolymer/aluminum adhesion to the study of model polyurethanes on 316L stainless steel. At present, the latter work involves the study of the simulated seawater corrosion (free and accelerated) of the stainless steel surface.
7. We have continued our collaboration with Professor Pireaux's group in Belgium in the quantitative understanding of HREELS vibrational spectroscopy of polymer surfaces. A paper was submitted and two others are in preparation.

f. Plans for next year's work

1. Extend collaborative surface analysis to other MIMI Polymer Science investigators and provide substrata for further biological adhesion measurements.

We are working to collaborate with Geesey's group, Quatrano group (to provide peptide modified fluoropolymers for adhesion assays). We have offered to collaborate with Rabolt and McCarthy as needed.

2. Continue synthesis and characterization of multicomponent block copolymers and blends and the study of solvent casting effects as a means to promote a controlled surface composition.
  3. Continue work on metal/fluoropolymer adhesion chemistry.
- g. List of names of graduate students and postdoctoral fellows currently working on this project.

Dr. Fabienne Fally, (ONR/NATO postdoctoral scholar) (female)

Hengzhong Zhuang, Graduate Student

Susan Kovatch, Graduate Student (female)

Marc Patterson, Graduate Student (minority graduate student)

Evan Bekos, Graduate Student

Jiaxing Chen, Graduate Student

Yuezhong Du, Graduate Student

Daniel Hook, Graduate Student

Patrick Schamberger, Completed Ph.D, now postdoc with Geesey at MSU

# **Part III**

## **Research Highlight**

**GRANT N0001493310058**

**R&T Code 4132083**

**Surface Chemistry of Non-Fouling Coating Polymeric  
Materials**

**J. A. Gardella, Jr. P.I.**

**SUNY Buffalo Department of Chemistry**

**Goals of Program**

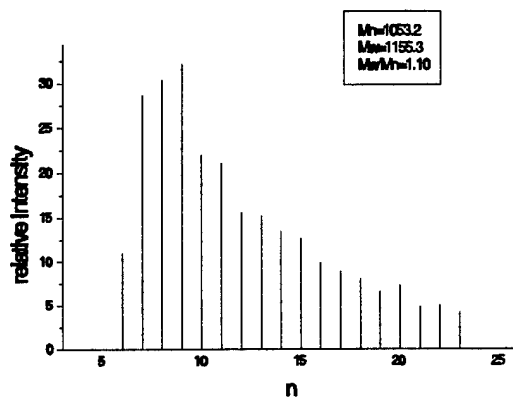
- 1. Develop New Surface Analytical Methods and Measurements for Multicomponent Polymers (i.e. candidate coating materials)**
- 2. Apply to Learn Why and How Successful Minimally Adhesive Surfaces Work (i.e. Silicone containing polymers)**
- 3. Synthesize Block Copolymers and Blends And Study Processing Effects on Surface Composition and Structure (both in our laboratory and in cooperation with other ONR sponsored investigators).**
- 4. Develop Measurements to Study Biological Macromolecule Structure and Conformation on Surfaces: Study Effect of Underlying Surface**
- 5. Study Metal Polymer Surface and Interfacial Chemistry for Strong Adhesion and Biocorrosion Protection**

The figure shown gives the apparent segment length distributions of siloxane segments at the surface of a solvent cast thick polymer film of two segmented siloxane poly-urea urethane copolymers (aka pU-pDMS). These data were determined by transforming Time of Flight Secondary Ion Mass Spectrometric data for pU-pDMS samples with nominal average segment length of 1000 D and 2400 D. The results show an equivalent segment length distribution between the two samples. This means that the surface of the materials contain the lower molecular weight segments preferentially.

This is the first report of the measurement of segment length distributions at the SURFACE of a solid polymer coating.

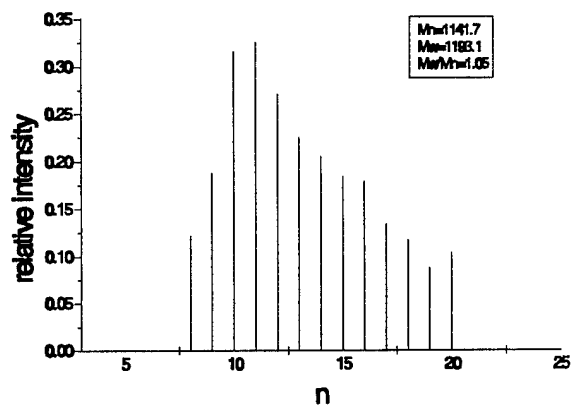


Molecular Weight Distribution of PDMS 1K  
(Thin film on a Ag substrate)



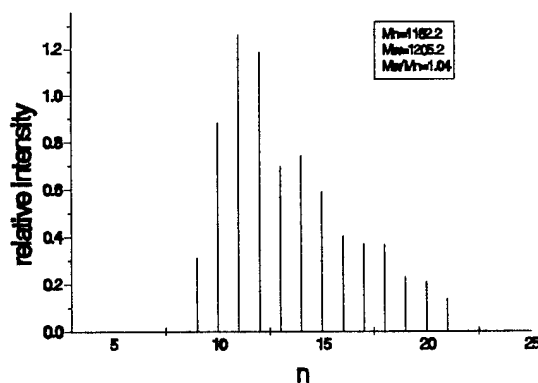
A. MWD data from submonolayer sample of pDMS,

Molecular Weight Distribution of PDMS Segments  
Segregated on the Surface of the PU-DMS No.1 Thick Film



B. MWD data from thick film sample 1, MW pDMS = 1000.

Molecular Weight Distribution of PDMS Segments  
Segregated on the Surface of the PU-DMS No.3 Thick Film



C. MWD data from thick film sample 1, MW pDMS = 2400..

## **Significance of Progress**

- 1. We have a means to determine the distribution of segment length molecular weights from thick films to determine the effects of structure, processing and marine exposure and degradation at polymer surfaces.**
- 2. We have continued and extended our ESCA in-depth profile technique to compare fluorocarbon-poly amide urethane copolymers with different structures. The topmost 10 nm can be revealed in terms of surface segregation of fluorocarbon chains and depth of depletion layers.**
- 3. The effects of simulated marine exposures on the metal polymer interface have been revealed for fluoropolymers: reactive metal interfaces will play a role in long term degradation.**